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Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films

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A negative isotropic magnetoresistance effect more than three orders of magnitude larger than the typical giant magnetoresistance of some superlattice films has been observed in thin oxide films of perovskite-like $La_{0.67}Ca_{0.33}MnO_x$. Epitaxial films that are grown on $LaAlO_3$ substrates by laser ablation and suitably heat treated exhibit magnetoresistance values as high as 127,000 percent near 77 kelvin and ~1300 percent near room temperature. Such a phenomenon could be useful for various magnetic and electric device applications if the observed effects of material processing are optimized. Possible mechanisms for the observed effect are discussed.

Giant magnetoresistance (GMR) caused by spin-dependent scattering in metallic multilayers (*1–5*), heterogeneous alloy films (*6*, *7*), and spinodally decomposed alloys (*8*) has attracted considerable attention in recent years for fundamental physics as well as device applications such as magnetic recording heads (*9*). The GMR effect is characterized not only by its large magnetoresistance (MR) ratio, typically −5 to −50% as compared to ~+3% for the 80% Ni–20% Fe type permalloy, but also by its negative value and isotropic (independent of field orientation) nature (*7*). The MR ratio is defined here as $\Delta R/R_H = (R_H - R_0)/R_H$, where R_0 is the resistance at a magnetic field of $H = 0$ and R_H is R at $H = 6$ T.

The largest reported value of $\Delta R/R_H$ for metallic materials was ~−150% for Fe-Cr multilayer films measured at 4.2 K (*4*). More recently, a large MR effect was also reported for naturally layer-structured materials, such as the intermetallic compound Sm-Mn-Ge (*10*), and the magnetic oxide films of perovskite-like Nd-Pb-Mn-O (*11*), La-Ba-Mn-O (*12*), and La-Ca-Mn-O (*13*). The La-Ba-Mn-O films gave a $\Delta R/R_H$ value of as large as −150% at room temperature, whereas the La-Ca-Mn-O films gave a value of ~−110% at ~220 K but ~0% at room temperature. The perovskite-like crystal structure of these compounds exhibit ferromagnetic ordering in the crystallographic *ab* planes (Mn-O layers), separated by nonmagnetic La(Ca)-O layers, and antiferromagnetic ordering along the *c* axis (*14*). The mixed Mn^{3+}-Mn^{4+} valence state in these compounds is responsible for the occurrence of both ferromagnetism and metallic conductivity (*15*, *16*).

We prepared epitaxial thin films of La-Ca-Mn-O, 1000 to 2000 Å thick, on (100) $LaAlO_3$ substrates by pulsed laser deposition. The target, with a nominal composition of $La_{0.67}Ca_{0.33}MnO_x$, was made by the mixing of high-purity component oxides or carbonates and repeated grinding and sintering at ~1000° to 1300°C for 16 hours in oxygen. The substrate temperature was maintained at 600° to 700°C during deposition. The deposition was carried out under 100 mtorr partial O_2 atmosphere.

The MR of the films, typically ~1000 Å thick, ~2 mm wide, and ~4 mm long, was measured by the four-point technique (at a constant current) in a superconducting magnet with the maximum applied field of 6 T. The direction of the field was the same as that of the current. Some of the samples were measured with the field perpendicular to the current direction, which showed the MR to have no obvious dependence on field orientation (that is, it is nearly isotropic) if the demagnetizing factor is taken into consideration. We obtained M-*H* loops with a vibrating sample magnetometer in a field of up to 1 T.

The chemical composition of the deposited films, as determined by scanning electron microscope microanalysis and Rutherford backscattering, was found to be essentially identical to that of the bulk target material used for the laser ablation deposition. The results of x-ray diffraction, rocking angle analysis, and transmission electron microscopy indicate that the films have a cubic crystal structure (lattice parameter $a \approx 3.89$ Å) and grow epitaxially on the (100) $LaAlO_3$ substrate ($a \approx 3.79$ Å).

The temperature dependence of the MR ratio for the as-deposited sample (substrate temperature, ~640°C) shows a high peak MR ratio of −460% near 100 K (Fig. 1). Subsequent annealing heat treatment moved the peak in the as-deposited film to a higher temperature with a narrower distribution. Processing at 700°C for 30 min in an O_2 atmosphere raised the peak temperature to ~200 K and gave a $\Delta R/R$ value of about −1400%. Processing optimizations have led to a further improved MR in excess of ~−100,000% near 77 K.

It is not clearly understood why the $\Delta R/R$ value and the peak temperature in the deposited films change with the heat-treatment temperature and time. Several possibilities include the effect of heat treatment on oxygen stoichiometry, epitaxy, defect density, chemical homogenization, and substrate-film chemical reactions.

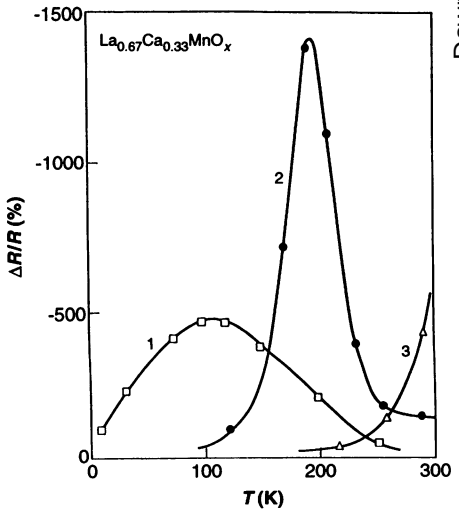

Fig. 1. Three MR ratio ($\Delta R/R_H$) versus temperature curves for the La-Ca-Mn-O films. Curve 1, as deposited; curve 2, heated to 700°C for 0.5 hour in an O_2 atmosphere; and curve 3, heated to 900°C for 3 hours in O_2.

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After 30 min of heat treatment at 700°C in an O_2 atmosphere, the electrical resistivity ρ of the film at 190 K rapidly decreased with the increasing field at the lower fields and then gradually decreased at a reduced rate at the higher fields. The $\Delta R/R_H$ (or $\Delta\rho/\rho_H$) value at $H = 6$ T is high, ~−1400% (this is equivalent to ~93.3% in terms of $\Delta R/R_0$, as is sometimes used). As the ρ versus H curve is still not saturated at $H = 6$ T, higher MR ratios are expected at higher fields. For practical applications, the low field MR behavior is of more interest. The initially rapid decrease in resistivity with field is thus a desirable feature. At low fields, the $\Delta R/R_H$ value in this unoptimized film is still significant, for example, ~17% at $H = 1000$ Oe, ~9% at $H = 500$ Oe, and ~5% at $H = 100$ Oe, substantially higher (albeit at below room temperature) than a few percent in the 80% Ni–20% Fe permalloy films. It is desirable to improve the characteristics of the material so that as high a MR ratio at room temperature can be achieved at as low a field as possible.

There is a cusp in the temperature-dependence curve of resistivity ρ (at $H = 0$) (Fig. 2), with the La-Ca-Mn-O film showing a semiconducting and metallic behavior, respectively, above and below the cusp temperature. The peak MR ratio typically occurs at a temperature of ~190 K (Fig. 2), which is lower than the temperature of the resistivity peak. This corresponds to the temperature range where the film is metallic in nature. The MR peak is almost always located on the left side of the resistivity peak and at a temperature where the resistivity is about one-half to two-thirds of its peak value.

The M-T curve (Fig. 2) shows a noticeable magnetization near room temperature (the magnetization of the films was measured at $H = 1$ T with the substrate contribution at each temperature subtracted from the total magnetization). As the temperature was lowered, the magnetization began to increase, eventually reaching a near saturation value at ~100 K. The peak in $\Delta R/R$ (Fig. 2) occurred at a temperature where the magnetization was substantial (M ~ 150 electromagnetic units per cubic centimeter), not where the magnetization went to zero. Because the spin-disorder scattering is usually maximum near the magnetic transition temperature ($M \approx 0$), the $\Delta R/R$ peak in the present film does not appear to be attributable to this scattering but rather to the change from semiconducting to metallic behavior.

Annealing heat treatment of the films in an O_2 atmosphere at a higher temperature not only raises the temperature of peak MR (Fig. 1) but also lowers the electrical resistivity and increases the magnetization near room temperature. After a heat treatment at 900°C for 3 hours in O_2, a $\Delta R/R$ value ($H_{max} = 6$ T) as high as ~−400% has been observed at ~280 K. Preliminary results from a La-Ca-Mn-O film prepared from the same laser ablation target but deposited at a higher O_2 partial pressure of 300 mtorr indicate that the MR value of ~1300% is obtained at ~260 K. These values are the highest known for any GMR or perovskite oxide–type materials near room temperature. The films are strongly ferromagnetic at ~280 K with $4\pi M$ (at $H = 1$ T) of ~2800 G and H_c (coercivity) of ~30 Oe.

An optimization of compound chemistry, thin-film deposition parameters, and heat treatment will most likely result in further improved MR properties in the La-Ca-Mn-O films. When the target disk used for laser ablation was prepared into a denser material by sintering at a higher temperature of 1300°C (instead of 1000° to 1100°C, as was used for the deposition of the samples of Figs. 1 and 2), higher quality films with less flaws (such as particulates and pores) and better epitaxy were obtained with much improved MR properties. We analyzed a La-Ca-Mn-O film near its peak MR temperature, ~77 K (liquid nitrogen temperature), with a sample that was heat-treated at 900°C for 0.5 hour in 3 atmospheres of O_2 (Fig. 3). A very large MR ratio of 127,000% (more than a thousandfold change in resistivity) was obtained as the resistivity dropped from 11.6 ohm·cm at $H = 0$ to 9.1 mohm·cm at $H = 6$ T. The major part of the resistivity drop occurred below ~2 T (Fig. 3). The fact that the electrical resistivity of the material can be manipulated to change by applied field to a value orders of magnitude different could be exploited for a variety of technical applications.

The temperature-dependent behavior of ρ, $\Delta R/R$, and M in this film was qualitatively similar to that shown in Fig. 2 except that the MR peak was at a lower temperature of ~77 K and the MR was much larger. The temperature of peak resistivity was ~95 K. Thus, as in Fig. 2, the peak MR occurred on the left side of the resistivity peak, where the film is metallic in nature, with a strong magnetic moment (M > 120 electromagnetic units per cubic centimeter).

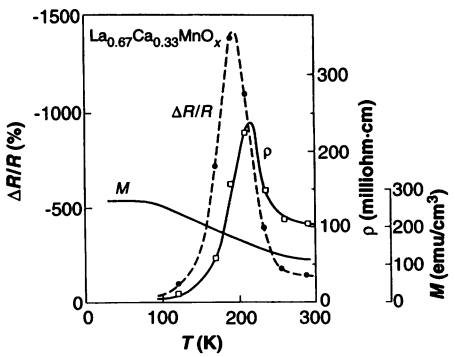

Fig. 2. Temperature dependence of $\Delta R/R$, ρ, and M after 750°C treatment for 0.5 hour.

The origin of the larger (by three orders of magnitude) MR effect in our La-Ca-Mn-O films as compared with the previously reported values on similar compounds (*12, 13*) may be attributable to a number of differences in composition and processing details. However, a good epitaxy, as demonstrated by the data in Fig. 3, appears to be one of the most important parameters for high MR, on the basis of the following additional data and observations: (i) Nonepitaxial (non–single crystalline) materials, such as bulk, polycrystalline samples of similar composition, yielded very low MR values of 40 to 100% in the 4.2 to 300 K temperature range (very low only in a relative sense). (ii) Nonepitaxial thin films prepared by deposition on substrates with a larger lattice mismatch, such as (100) MgO or Si, also exhibited very low MR values of less than ~200%. This data may explain the low MR values recently reported by Chahara *et al.* (*13*) in La-Ca-Mn-O films deposited on MgO substrates. (iii) von Helmolt *et al.* (*12*) reported a relatively low MR value of ~150% in La-Ba-Mn-O films which was the same value as in their bulk polycrystalline samples (and is also comparable to those in our polycrystalline materials). This very low MR value in the La-Ba-Mn-O films could possibly be the result of insufficient epitaxy introduced in the films, although the possibility of La-Ba-Mn-O being inherently inferior to La-Ca-Mn-O in MR behavior cannot be ruled out.

The reason the presence of grain boundaries in bulk materials, nonepitaxial films, or poorly epitaxial films seems to deteriorate the MR properties is still being investigated.

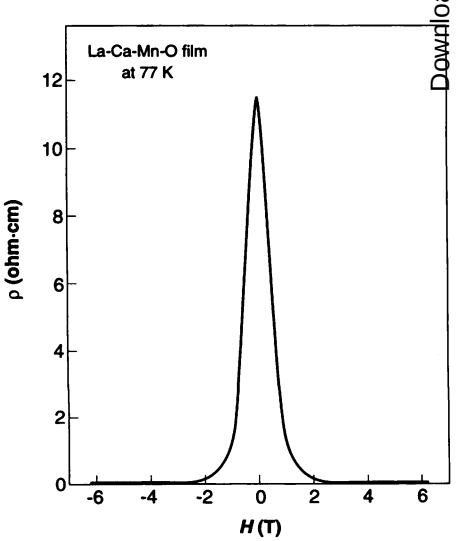

Fig. 3. A ρ versus H curve after heating to 900°C for 0.5 hour. $R_0 = 1.35$ megohms, $\rho_0 = 11.6$ ohm·cm, $R_{6\ T} = 1.06$ kohms, $\rho_{6\ T} = 9.1$ mohm·cm, $\Delta R/R_H \approx 127{,}000\%$, and $\Delta R/R_0 \approx 99.9\%$.

high electrical resistivity is a prerequisite to the occurrence of large MR values in the La-Ca-Mn-O material. The bulk, polycrystalline materials are too conductive ($\rho < 50$ mohm·cm at 4.2 to 300 K) to give very large MR. Whether the grain boundaries in the present manganite perovskites behave like "weak links," shorting out the intragranular regions with larger MR properties, needs to be investigated. It would be interesting to compare the differences in MR behavior of single crystals, polycrystals, and epitaxial thin films of these manganates in analogy to the differences in critical current behavior among the same three types of material configurations in cuprate perovskite-based, high–transition temperature superconductors such as La-Ba-Cu-O or Y-Ba-Cu-O. In the cuprate superconductors, the presence or absence of grain boundaries (weak links) and flux-trapping defects results in dramatic differences in transport properties, especially in high magnetic fields (*17*), with the epitaxial thin films exhibiting about two orders of magnitude higher critical currents than the single crystals, which in turn show values many orders of magnitude larger than those of the polycrystalline bulk materials.

Aside from the orders of magnitude larger MR effect, the mechanism of MR in the present, single-phase, single crystalline oxide films is entirely different from the GMR mechanism, which is mostly the spin-dependent scattering involving the interfaces in multilayered or heterogeneous metal films. The exact mechanisms responsible for the observed MR in La-Ca-Mn-O are not clearly understood at the moment, although it seems to be related to the semiconductor-metal transition. Some possible mechanisms, such as the spin-dependent electron scattering attributable to the field-induced change in the canting angle of manganese spins, magnetic polaron hopping, and critical magnetic scattering, have been proposed (*11–13*). However, the fact that the peak in $\Delta R/R$ in the present films occurs not near the magnetic transition temperature but in the temperature region where the magnetization is already substantial suggests that the spin-disorder scattering is not the main mechanism. The highly magnetoresistive behavior in the La-Ca-Mn-O films of Figs. 2 and 3 may be related to that in ferromagnetic semiconductors, for example, EuO crystals, where the peak MR occurs after the semiconductor-to-metal transition (*18*). Further work is needed to pinpoint the underlying mechanisms for the observed GMR behavior.

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Adhesion Forces Between Individual Ligand-Receptor Pairs

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The adhesion force between the tip of an atomic force microscope cantilever derivatized with avidin and agarose beads functionalized with biotin, desthiobiotin, or iminobiotin was measured. Under conditions that allowed only a limited number of molecular pairs to interact, the force required to separate tip and bead was found to be quantized in integer multiples of 160 ± 20 piconewtons for biotin and 85 ± 15 piconewtons for iminobiotin. The measured force quanta are interpreted as the unbinding forces of individual molecular pairs.

Specific molecular interaction is a distinguishing aspect of the life sciences. Such interactions, derived from multiple weak bonds between geometrically complementary surfaces of recognition sites, are short-range, noncovalent, and can be very strong. Examples are molecular recognition between receptor and ligand, antibody and antigen, and complementary strands of DNA. Attempts to investigate the forces that characterize these interactions have been limited by the lack of suitable techniques to measure the forces between individual molecules. Although the optical trapping technique is very sensitive, its use has been limited to certain samples and to measurements of forces less than tens of piconewtons and it is not suitable for studies where greater applied forces are needed (*1*). Magnetic force experiments (*2*), pipette suction experiments (*3*), and experiments with the surface force apparatus (*4*) are sensitive but lack spatial resolution. With the development of the scanning probe microscopes, particularly the atomic force microscope (AFM), new instruments and techniques have become available that have the precision and sensitivity to probe surfaces in physiological environments with molecular resolution and at forces down to the piconewton range (*5*).

Here we used an AFM to measure the specific interaction between biotin and avidin, a 67-kD protein with four identical subunits (*6*). We chose this ligand-receptor pair as a model system because of its high affinity,

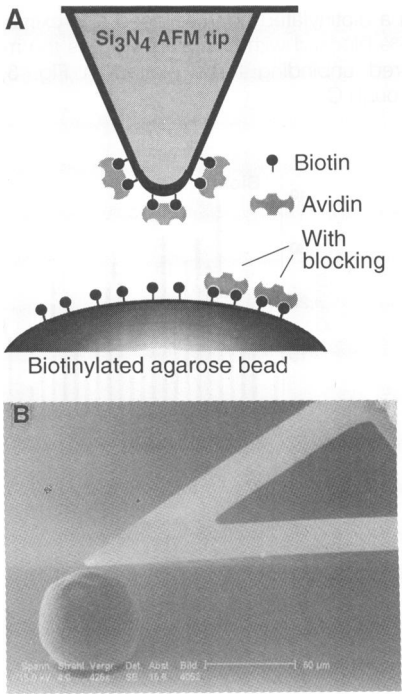

Fig. 1. (**A**) Schematics of the avidin-functionalized AFM tip and the biotinylated agarose bead, shown here partially blocked with avidin. (**B**) Scanning electron micrograph of an AFM cantilever on an agarose bead.

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